

## CHAPTER IV

### RESULTS AND DISCUSSION

#### 4.1 Adsorbent Characterizations

##### 4.1.1 Surface Area Analysis

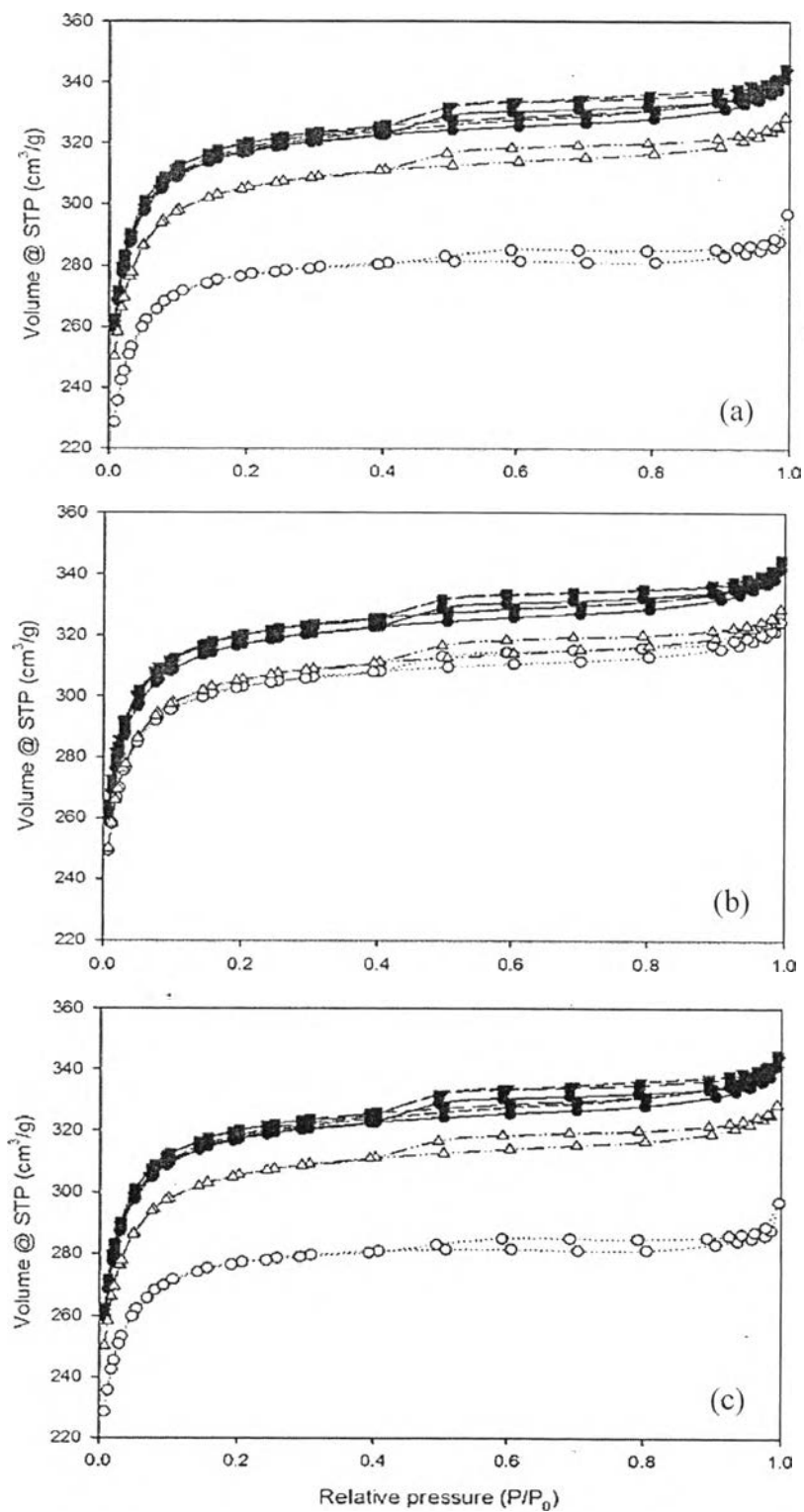
Activated carbons used in the study were produced from coconut shell and chemical surface treatment, which inherently affect their ability to adsorb methane and carbon dioxide. Nitrogen adsorption-desorption isotherms of the adsorbents were conducted using an Autosorb-1MP (Quantachrome Instrument). The adsorbents were previously degassed at 300 °C, and the study was carried out at the liquid nitrogen temperature, -196 °C. The specific surface area was calculated with the Brunauer, Emmet, and Teller (BET) method, and the pore size distribution was obtained by Dubinin-Astakhov, DA method. The total pore volume was estimated from the adsorption of nitrogen at the relative pressure of 0.99. In this study, CSAC is referred to coconut shell activated carbon.

Table 4.1 summarizes the BET surface area, total pore volume, micropore volume, and average pore diameter of the adsorbents. The CSAC was also treated by alkali solutions, which were KOH and NH<sub>4</sub>OH. The samples are denoted as KOH/CSAC and NH<sub>4</sub>OH/CSAC, respectively. The surface areas of KOH/CSAC and NH<sub>4</sub>OH/CSAC are 962 and 963 m<sup>2</sup>/g. There is no significant change in the BET surface area. The alkali solutions are a weak oxidizing reagent, so they do not change the surface area, but only clean the activated carbon surface. After adding methyltriethoxysilane (MTES), there is also no significant change in the BET surface area. MTES was used to react with hydroxyl (-OH) group on the adsorbent surface to generate hydrophobic surface. It should be noted that the micropore volume, total pore volume, and average pore diameter of the adsorbents after treatment are the same.

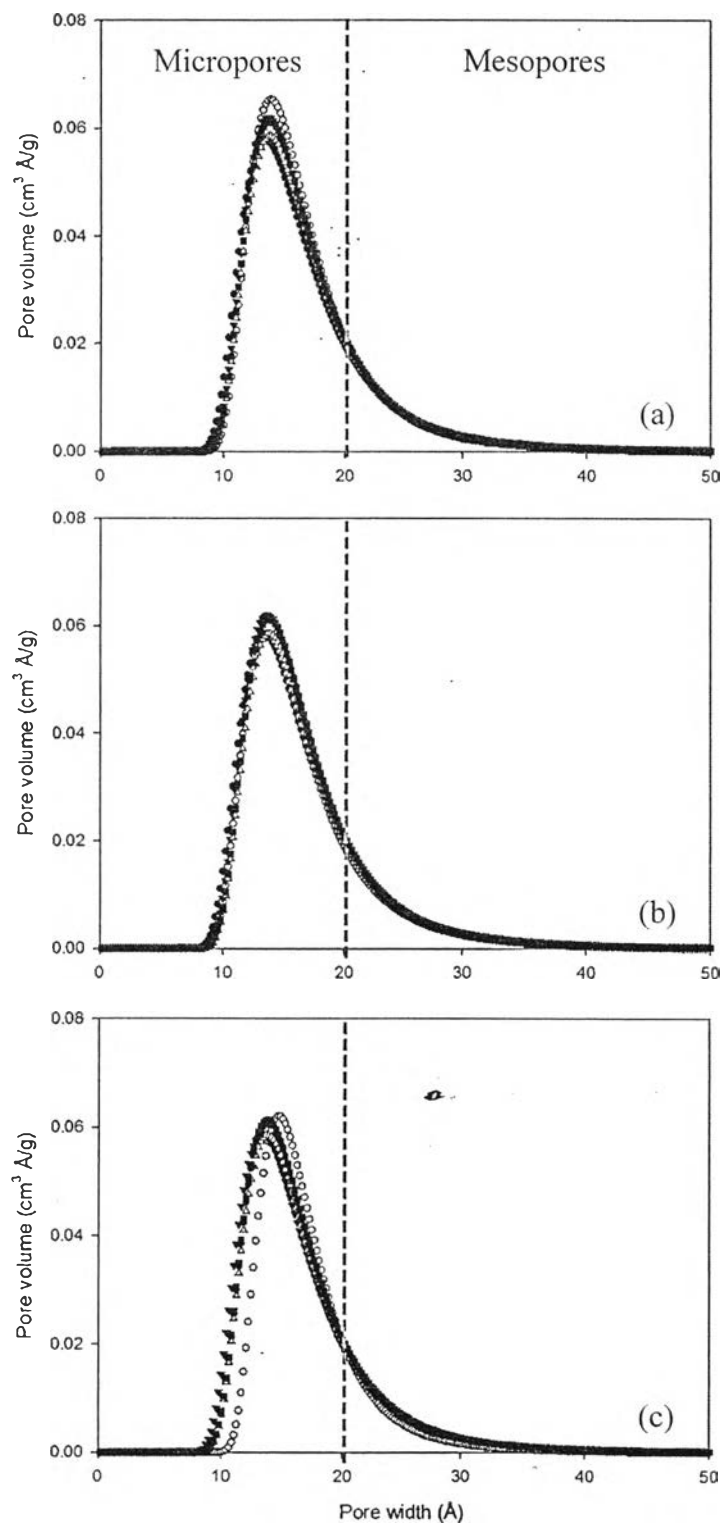
**Table 4.1** BET surface area, micropore volume, and average pore diameter of investigated adsorbents

Adsorbent	Physical Characterization			
	BET surface area (m <sup>2</sup> /g)	Micropore volume (cm <sup>3</sup> /g)	Total pore volume (cm <sup>3</sup> /g)	Average pore diameter (Å)
CSAC	952	0.51	0.52	13.40
CSAC – 0.005%MTES	976	0.52	0.54	13.80
CSAC – 0.010%MTES	976	0.52	0.53	13.60
CSAC – 0.020%MTES	972	0.52	0.53	13.70
CSAC – 0.030%MTES	970	0.51	0.52	13.70
KOH/CSAC	962	0.52	0.53	13.40
KOH/CSAC – 0.005%MTES	955	0.50	0.51	13.60
KOH/CSAC – 0.010%MTES	960	0.52	0.53	13.60
KOH/CSAC – 0.020%MTES	958	0.50	0.51	13.70
KOH/CSAC – 0.030%MTES	961	0.52	0.53	13.70
NH <sub>4</sub> OH/CSAC	963	0.51	0.53	13.70
NH <sub>4</sub> OH/CSAC – 0.005%MTES	959	0.50	0.52	14.70
NH <sub>4</sub> OH/CSAC – 0.010%MTES	960	0.52	0.53	13.40
NH <sub>4</sub> OH/CSAC – 0.020%MTES	959	0.51	0.52	13.70
NH <sub>4</sub> OH/CSAC – 0.030%MTES	961	0.52	0.53	13.70

Figure 4.1 shows N<sub>2</sub> adsorption isotherms on the adsorbents at -196 °C. The shape of the isotherms shows the characteristics of micropore solid. The hysteresis loop can be seen from the nitrogen adsorption-desorption isotherms. The loop is usually associated to the narrow slit-shaped pores (Rouquerol *et al.*, 1999).



**Figure 4.1** N<sub>2</sub> adsorption isotherms for (a) CSAC, (b) KOH/CSAC, and (c) NH<sub>4</sub>OH/CSAC; 0.000%MTES (●), 0.005%MTES (○), 0.010%MTES (▼), 0.020%MTES (Δ), and 0.030%MTES (■).



**Figure 4.2** Pore size distribution for (a) CSAC, (b) KOH/CSAC, and (c) NH<sub>4</sub>OH/CSAC; 0.000%MTES (●), 0.005%MTES (○), 0.010%MTES (▼), 0.020%MTES (△), and 0.030%MTES (■).

Figure 4.2 shows the pore size distribution (PSD) of the adsorbents derived from the N<sub>2</sub> adsorption isotherms using the Dubinin-Astakhov method. The entire adsorbents exhibit pores in the range between 10 and 30 Å, being micropores and mesopores. It can confirm the hysteresis loops of the nitrogen isotherms due to their small amount of mesopores. It can also be seen that the all activated carbons are microporous materials. Alcañiz-Monge *et al.* (1997) and Lozano-Castello *et al.* (2002) reported that the micropore is the size of porosity useful for methane storage applications. Regarding methane adsorption capacity, it is known that a reasonably linear relationship exists between micropore volume and methane uptake. The advanced ANG adsorbent needs to have micropore volume near 50%, solid carbon near 40%, and mesopores and macropores volume near 10% (Vasiliev *et al.*, 2000).

#### 4.1.2 CHN Analysis

The untreated and treated CSAC were analyzed for the quantities of carbon, hydrogen, nitrogen, and oxygen by the CHN analyzer (CHN2000). Table 4.2 summarizes the element quantities of C, H, N, and O of the adsorbents.

**Table 4.2** Elemental quantities of C, H, H, and O

Adsorbent	Element quantities (%w/w)			
	C	H	N	O
CSAC	73.0	3.66	0.00	23.34
KOH/CSAC	78.5	2.67	0.00	18.83
NH <sub>4</sub> OH/CSAC	86.6	2.84	0.21	10.35

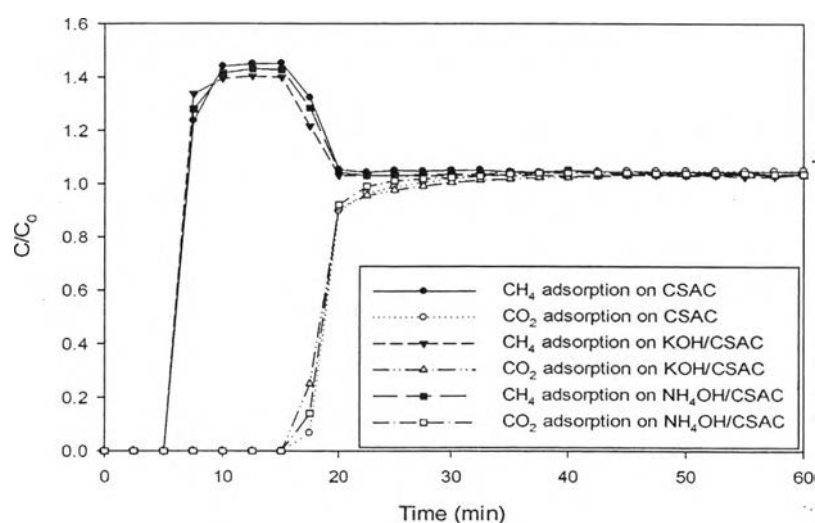
Table 4.2 shows the quantities of C, H, N, and O before and after treatment with KOH and NH<sub>4</sub>OH. The result shows that the quantities of C increase after treatment, while the quantities of O decrease because the adsorbents are oxidized by alkali solutions to remove inorganic and other impurities inside the pores. That affects to the oxygen containing groups, which are neutralized. Moreover, the quantities of C increase due to the proportion of C to all of the

components are increased. The quantities of N increase after treatment with  $\text{NH}_4\text{OH}$  because some elements of N might remain on surface of the adsorbent. This may affect the increase in the carbon dioxide adsorption capacity.

## 4.2 Methane and Carbon Dioxide Adsorption and Desorption on CSACs

### 4.2.1 Competitive Adsorption

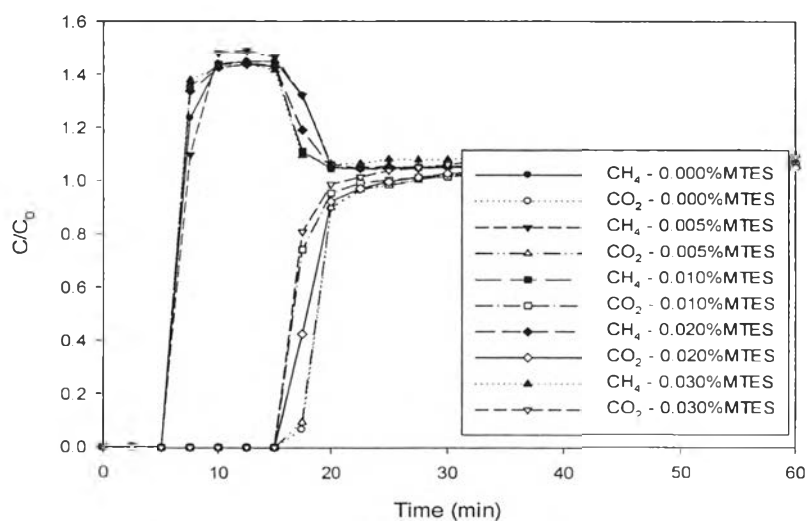
Investigation on the adsorption kinetics of methane and carbon dioxide was carried out in a stainless steel packed bed column with an inside diameter of 7.0 mm at atmospheric pressure and room temperature. Various adsorbents including untreated CSAC, CSAC treated by potassium hydroxide, and CSAC treated by ammonium hydroxide were studied. Methane and carbon dioxide composition were fixed at 10 vol% of the total feed gases. The kinetic adsorption and desorption curves of methane and carbon dioxide were plotted in terms of concentration ratio versus time, as shown in Figures 4.3.



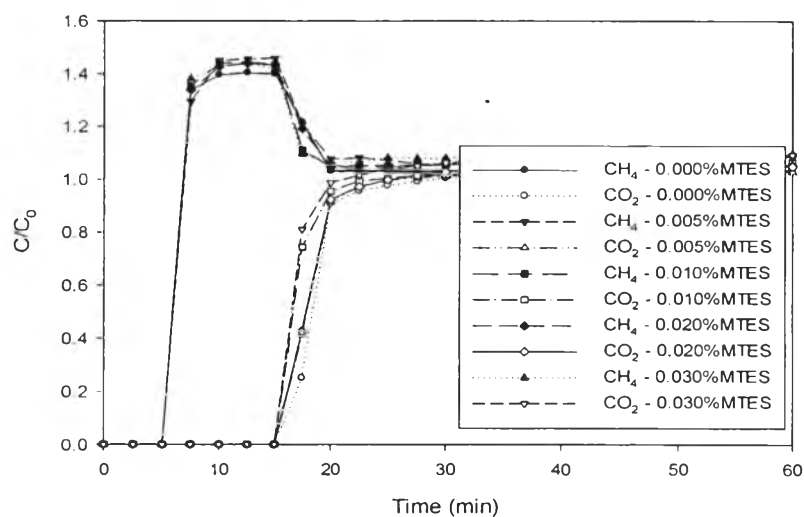
**Figure 4.3** Breakthrough curves of methane and carbon dioxide from the competitive adsorption on the untreated CSAC, treated by potassium hydroxide, and treated by ammonium hydroxide at room temperature.

From Figure 4.3, it can be seen that methane breaks through first at about 5 min, followed by carbon dioxide at approximately 15 min from all of the adsorbents. Methane roll up can be observed. The roll up reaches the highest concentration ratio at approximately 1.4 before it reverts to the equilibrium at about 20 min. The roll up is commonly observed because of the displacement of a relatively weakly adsorbed component on the CSAC, methane, by a more strongly adsorbed component, carbon dioxide. As the result of the surface treatment method on the CSAC by potassium hydroxide and ammonium hydroxide, the inorganic or other impurities inside the pore could be removed, and the treatment may also open the active pores, as seen in Table 4.1. In 2005, Wu and coworkers studied the development of the activated carbon surface by the chemical activation of activated charcoal with potassium hydroxide. It was found that potassium hydroxide could develop micropores, which can enhance the adsorption of methane and carbon dioxide. Under the alkaline environment, it is expected to have the formation of oxygen functional groups on the surface of activated carbon. The adsorption properties of porous carbon materials are defined not only by the porous structure but also by the presence of surface chemical functionalities that could be different by the nature of the starting materials and the preparation conditions applied.

The MTES was used as a hydrophobic promoter on untreated CSAC, CSAC treated by potassium hydroxide, and CSAC treated by ammonium hydroxide with varying of the MTES concentration at 0.005, 0.010, 0.020, and 0.030 wt% of adsorbents. Methane and carbon dioxide compositions were fixed at 10 vol% of total feed gases. The adsorption and desorption curves of methane and carbon dioxide were plotted in terms of concentration ratio versus time at atmospheric pressure and room temperature, as shown in Figures 4.4 to 4.6.

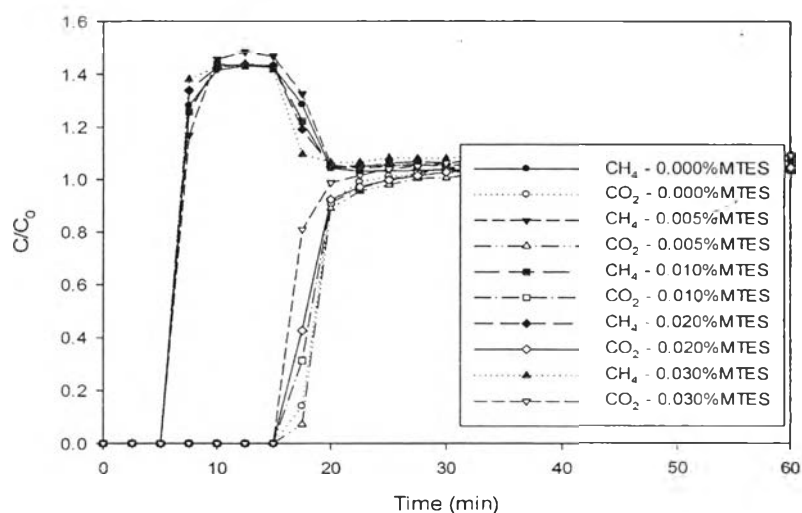


**Figure 4.4** Breakthrough curves of methane and carbon dioxide from the competitive adsorption on the untreated CSAC modified by MTES with 0.000, 0.005, 0.010, 0.020, and 0.030 wt% at room temperature.



**Figure 4.5** Breakthrough curves of methane and carbon dioxide from the competitive adsorption on the CSAC treated by potassium hydroxide and modified by MTES with 0.000, 0.005, 0.010, 0.020, and 0.030 wt% at room temperature.





**Figure 4.6** Breakthrough curves of methane and carbon dioxide from the competitive adsorption on the CSAC treated by ammonium hydroxide and modified by MTES with 0.000, 0.005, 0.010, 0.020, and 0.030 wt% at room temperature.

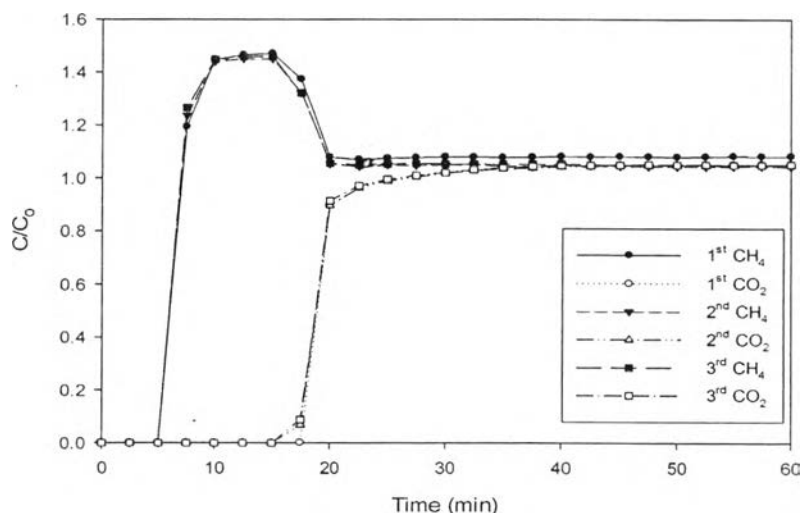
The breakthrough curves of methane and carbon dioxide from the adsorption shows that methane also breakthroughs first at 5 min similar to the breakthrough curves of both gases before adding of MTES, followed by carbon dioxide at 15 min. The breakthrough curves of carbon dioxide on the adsorbents, which were added with 0.010 wt% and 0.030 wt% MTES onto the untreated CSAC, have higher slope before reaching to equilibrium than that of adding 0.020 wt% MTES. That is similar to the carbon dioxide breakthrough curves of the KOH/CSAC with 0.010 wt% and 0.030 wt% MTES. The NH<sub>4</sub>OH/CSAC shows the highest slope of the carbon dioxide breakthrough curves at 0.030 wt% MTES. The slope of breakthrough curves represents the amount of adsorbed gases. The adsorption increases with the increase in the slope of the breakthrough curves. Therefore, the carbon dioxide adsorption is lower in the untreated CSAC and the KOH/CSAC with 0.010 and 0.030 wt% MTES and the NH<sub>4</sub>OH/CSAC with 0.030 wt% MTES than the other modified adsorbents.

The MTES acts as a hydrophobic promoter, which reacts with the OH groups on the activated carbon surface, and then form alcohol. By controlling the

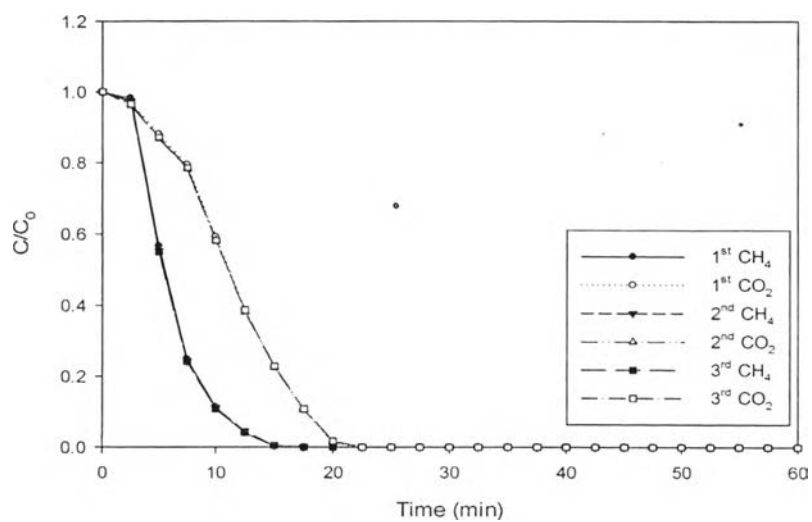
reactions of MTES, the inorganic and organic materials that originally have low affinity with each other can have high adhesiveness. On the contrary, if the reaction of the MTES is inappropriate, the adhesion strength may decrease. Therefore, it is very important to control the reaction so that it is appropriate.

#### 4.2.2 Adsorbent Stability

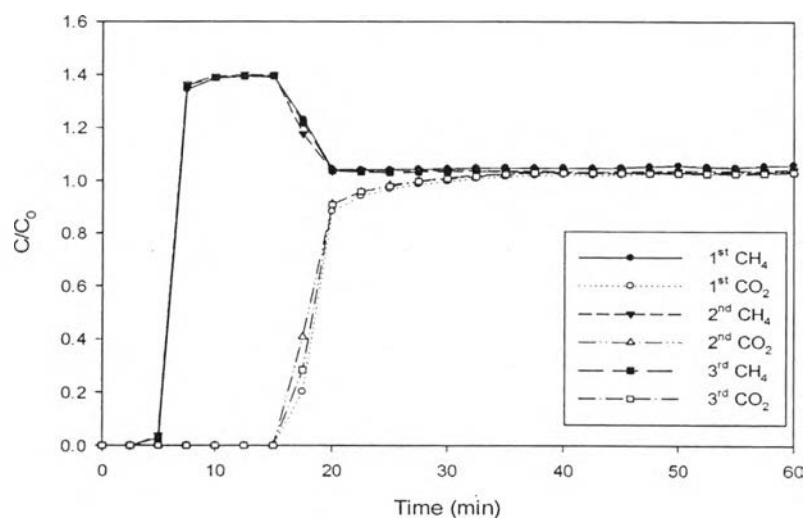
The adsorbent stability was studied by the 3-cycle adsorption-desorption process of methane and carbon dioxide. After finishing the adsorption process, a flowrate of methane and carbon dioxide was shut-off and the flowrate of helium gas was increased to remove adsorbates from the adsorbent surface. The removed adsorbates were detected by GC-TCD and desorption curves were also plotted in terms of concentration ratio versus time. The untreated CSAC, CSAC treated by potassium hydroxide, and CSAC treated by ammonium hydroxide were studied the stability at atmospheric pressure and room temperature with the initial concentration of methane at 10 vol% and carbon dioxide at 10 vol%. are shown in Figures 4.7 to 4.12.



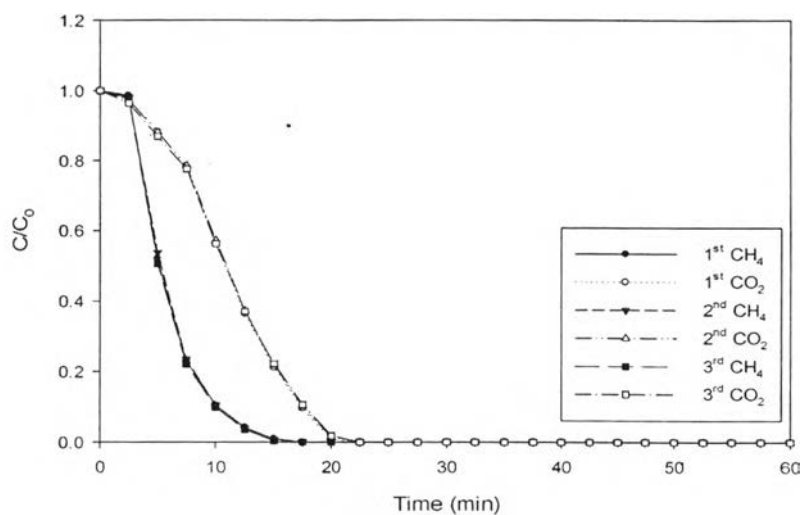
**Figure 4.7** Breakthrough curves of methane and carbon dioxide from the 3-cycle adsorption process on untreated CSAC at room temperature.



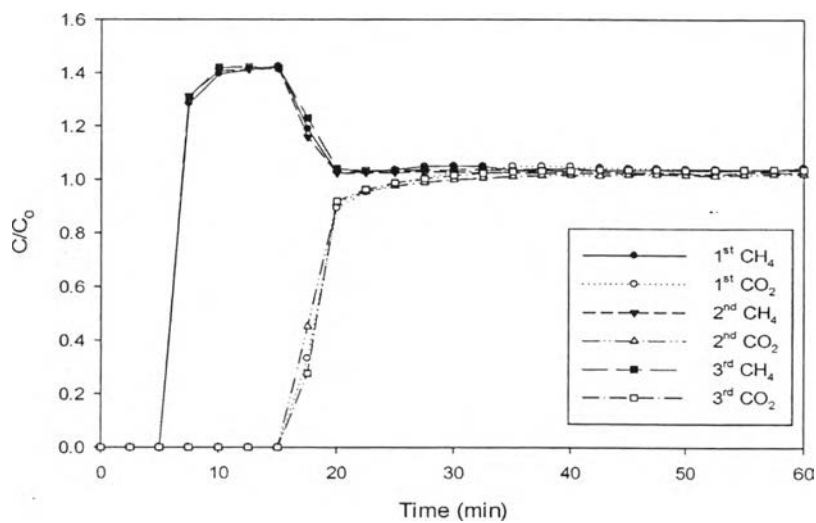
**Figure 4.8** Three desorption cycles of methane and carbon dioxide on untreated CSAC at room temperature.



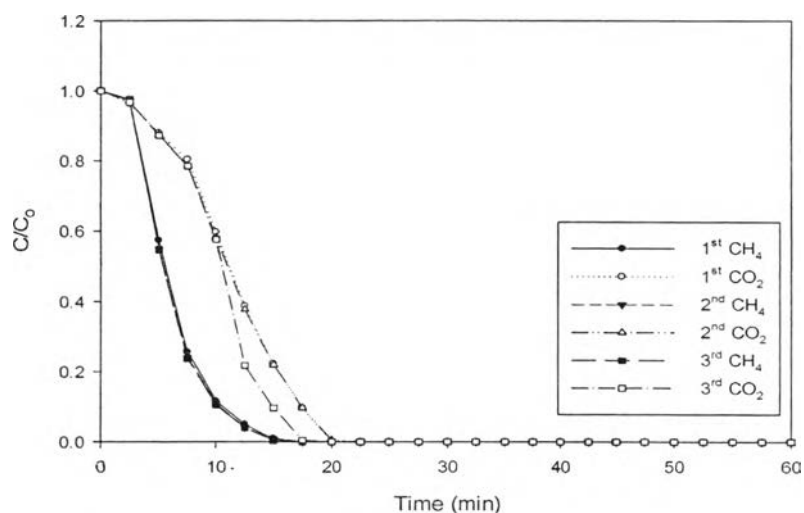
**Figure 4.9** Breakthrough curves of methane and carbon dioxide from the 3-cycle adsorption process on CSAC treated by potassium hydroxide with impregnation ratio 1:1 at room temperature.



**Figure 4.10** Three desorption cycles of methane and carbon dioxide on CSAC treated by potassium hydroxide with impregnation ratio 1:1 at room temperature.



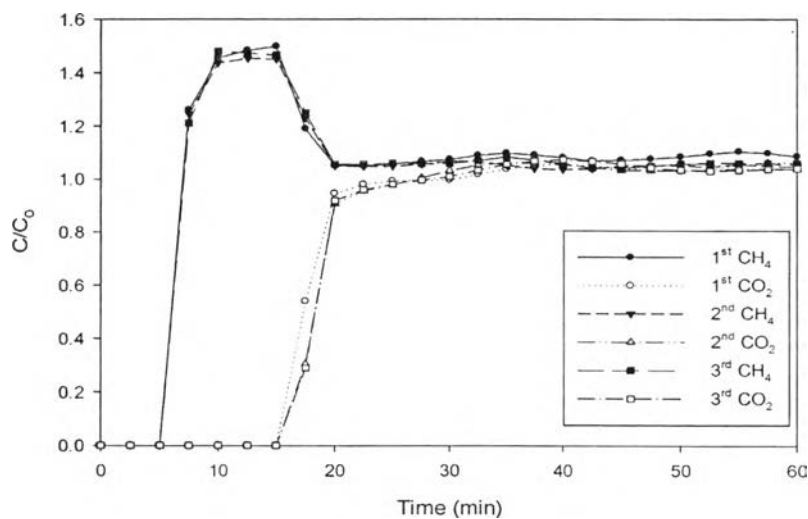
**Figure 4.11** Breakthrough curves of methane and carbon dioxide from the 3-cycle adsorption process on CSAC treated by ammonium hydroxide with impregnation ratio 1:1 at room temperature.



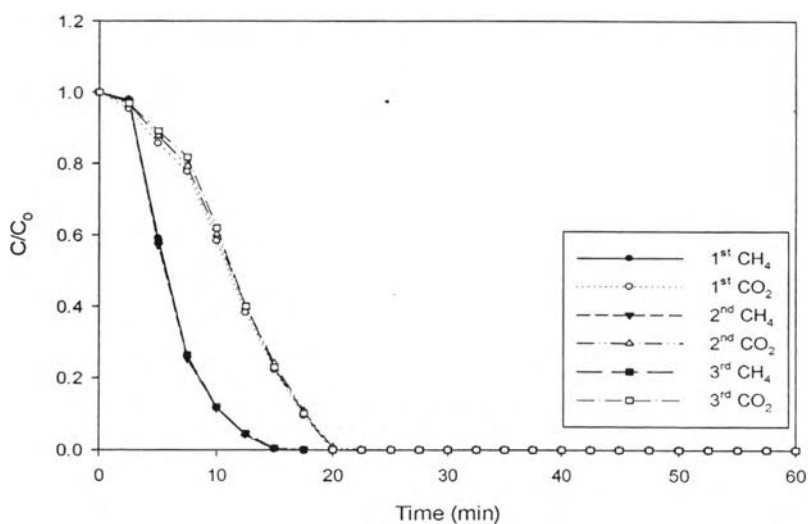
**Figure 4.12** Three desorption cycles of methane and carbon dioxide on CSAC treated by ammonium hydroxide with impregnation ratio 1:1 at room temperature.

The adsorption – desorption cycles of methane and carbon dioxide from the regenerated adsorbents shows the same breakthrough patterns for all adsorbents. The results indicate that the stability of the untreated CSAC, CSAC treated by potassium hydroxide, and CSAC treated by ammonium hydroxide is hardly affected by the increase in the adsorption cycle, as seen in Figures 4.10, 4.12, and 4.14, respectively. It has no difference in the breakthrough curves and the breakthrough times of both gases during its regeneration cycles. This could be due to its cleaner surface after the treatment that allows the feed gas molecules to adsorb and desorb easily. It is likely that no gas molecules remain and block the active pores after the regeneration cycles.

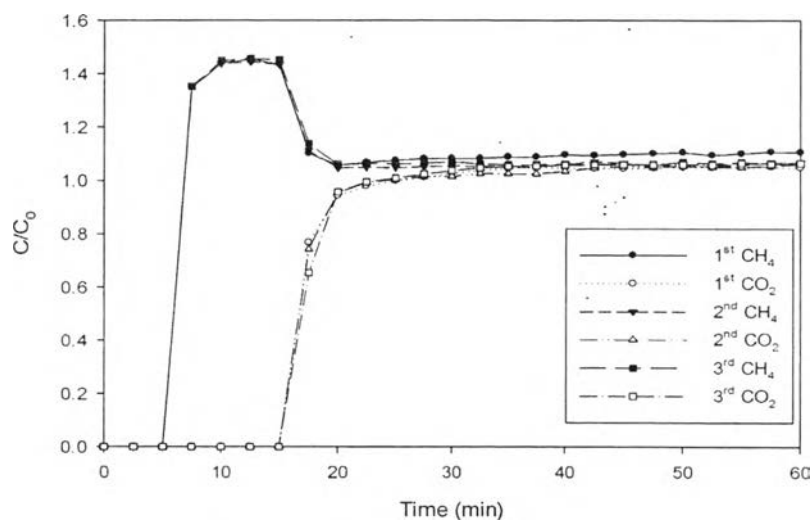
The adsorbent stability was also studied by the 3-cycle adsorption and desorption process of methane and carbon dioxide on modified CSAC by MTES at atmospheric pressure and room temperature with the same initial concentration of methane and carbon dioxide at 10 and 10 vol%. The breakthrough curves and desorption cycles of methane and carbon dioxide on the investigated adsorbents for the three cycles are shown in Figures 4.13 to 4.36.



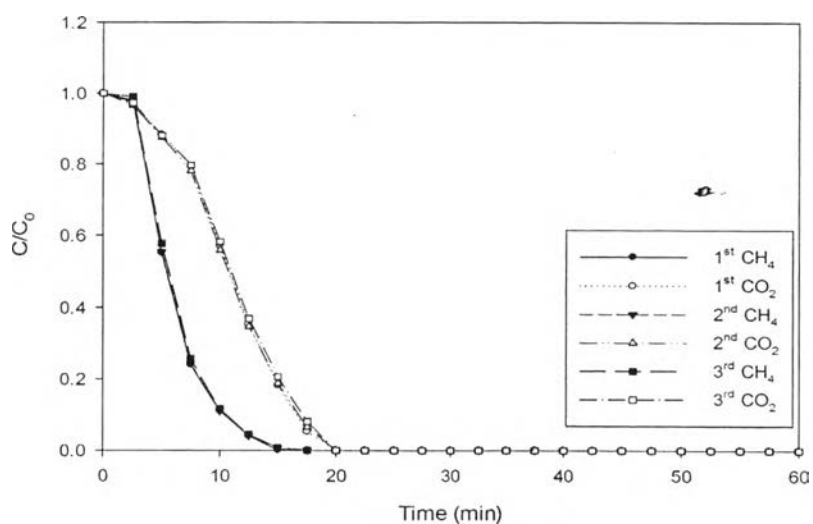
**Figure 4.13** Breakthrough curves of methane and carbon dioxide from the 3-cycle adsorption process on the untreated CSAC with 0.005 wt% MTES at room temperature.



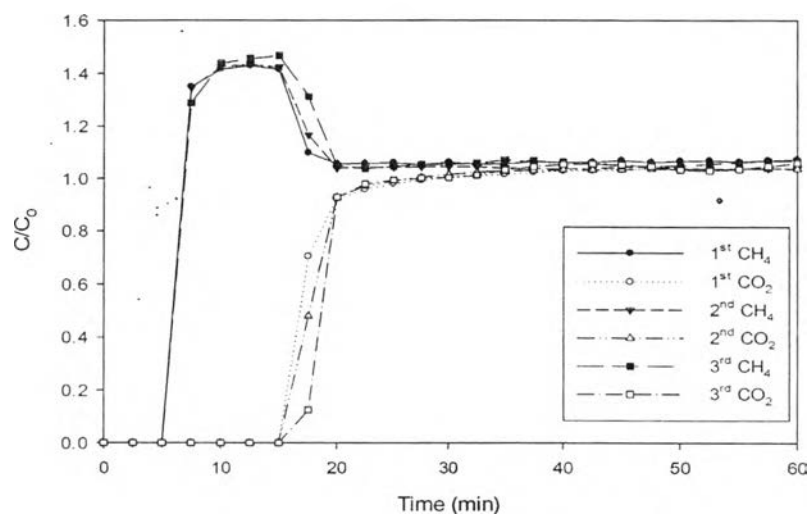
**Figure 4.14** Three desorption cycles of methane and carbon dioxide on the untreated CSAC with 0.005 wt% MTES at room temperature.



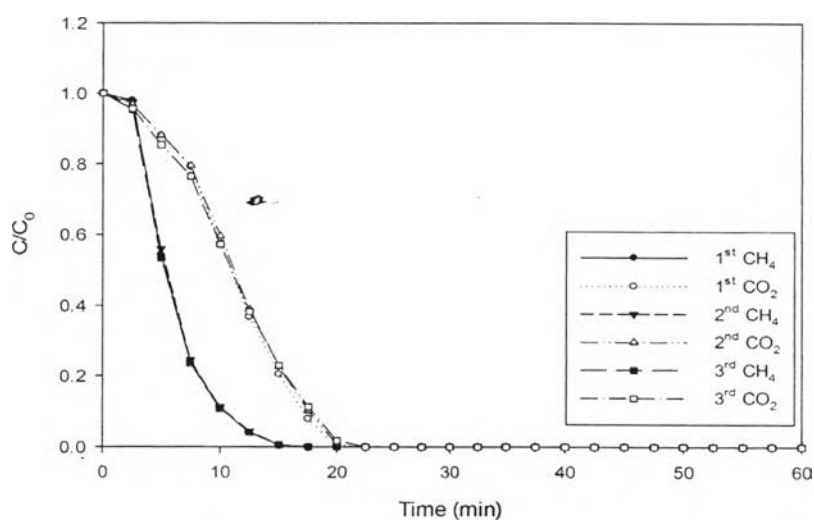
**Figure 4.15** Breakthrough curves of methane and carbon dioxide from the 3-cycle adsorption process on the untreated CSAC with 0.010 wt% MTES at room temperature.



**Figure 4.16** Three desorption cycles of methane and carbon dioxide on the untreated CSAC with 0.010 wt% MTES at room temperature.

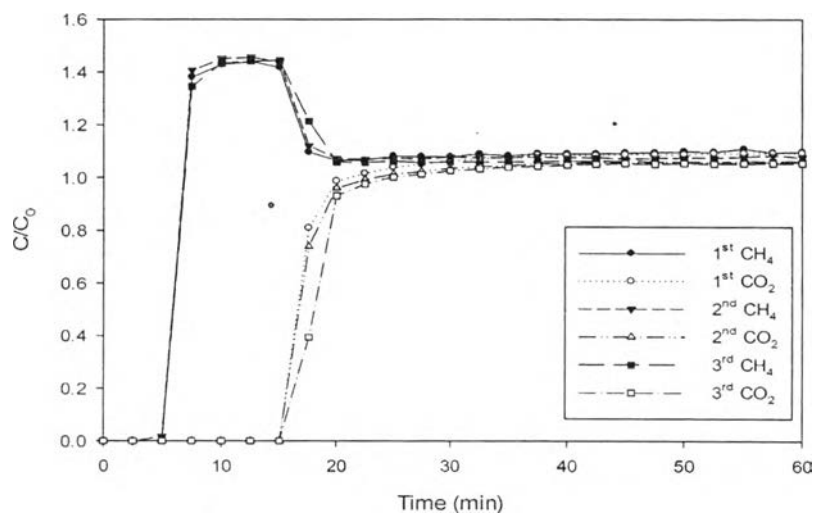


**Figure 4.17** Breakthrough curves of methane and carbon dioxide from the 3-cycle adsorption process on the untreated CSAC with 0.020 wt% MTES at room temperature.

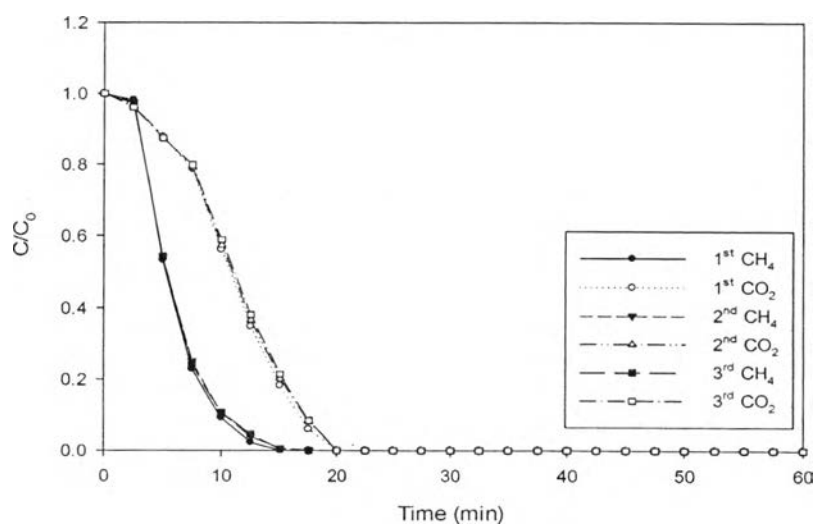


**Figure 4.18** Three desorption cycles of methane and carbon dioxide on the untreated CSAC with 0.020 wt% MTES at room temperature.

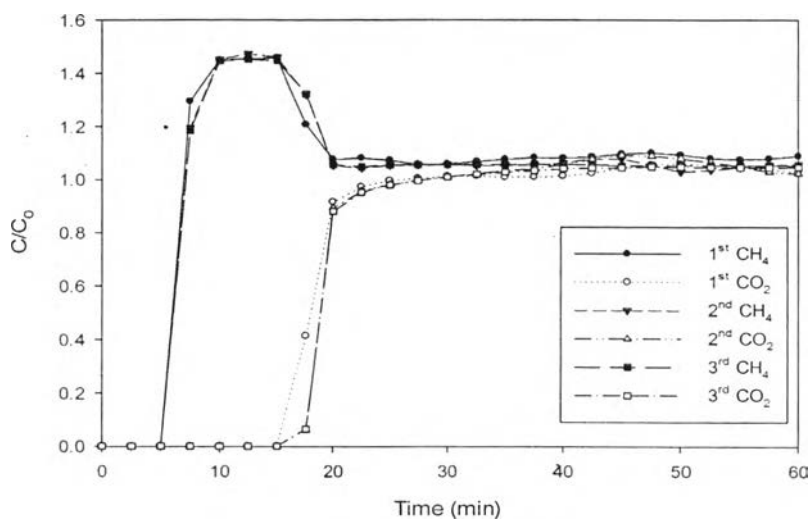




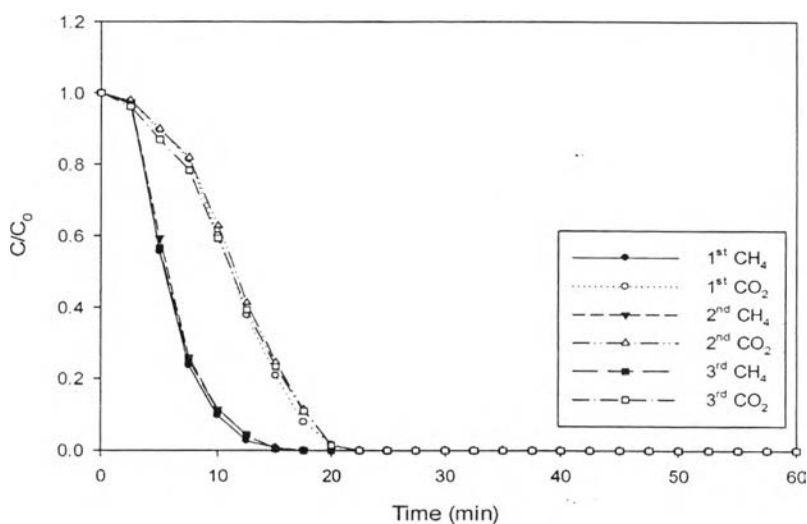
**Figure 4.19** Breakthrough curves of methane and carbon dioxide from the 3-cycle adsorption process on the untreated CSAC with 0.030 wt% MTES at room temperature.



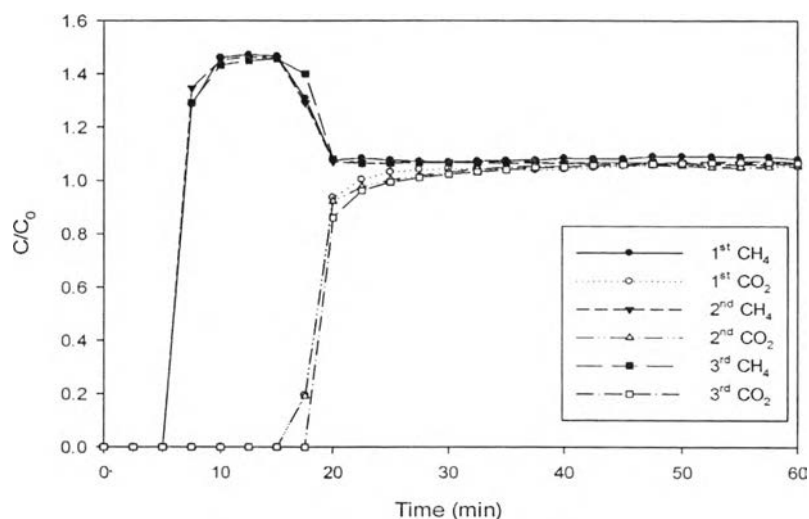
**Figure 4.20** Three desorption cycles of methane and carbon dioxide on the untreated CSAC with 0.030 wt% MTES at room temperature.



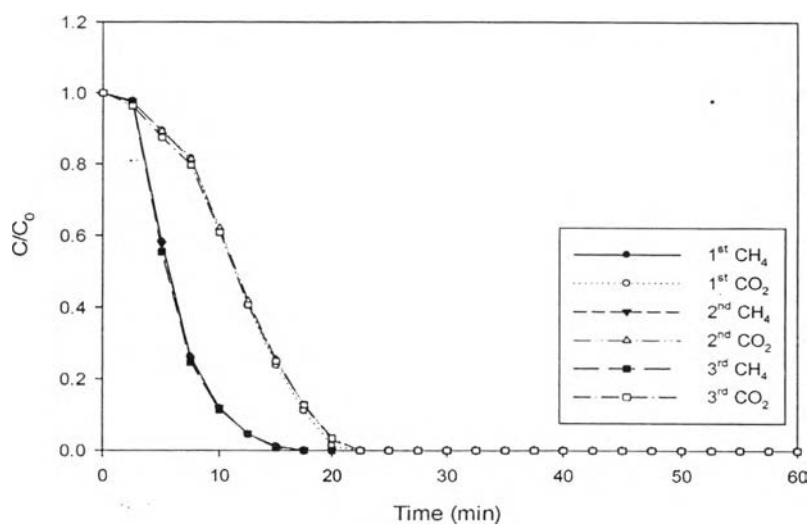
**Figure 4.21** Breakthrough curves of methane and carbon dioxide from the 3-cycle adsorption process on the CSAC treated by potassium hydroxide and modified by 0.005 wt% MTES at room temperature.



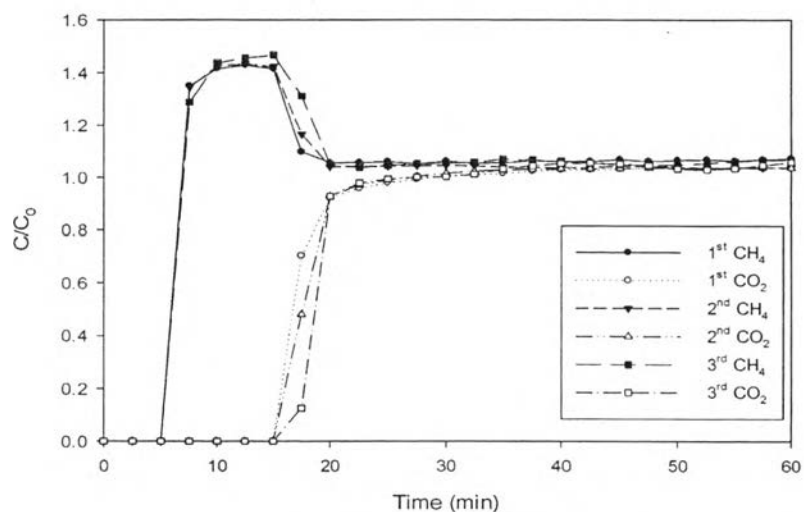
**Figure 4.22** Three desorption cycles of methane and carbon dioxide on the CSAC treated by potassium hydroxide and modified by 0.005 wt% MTES at room temperature.



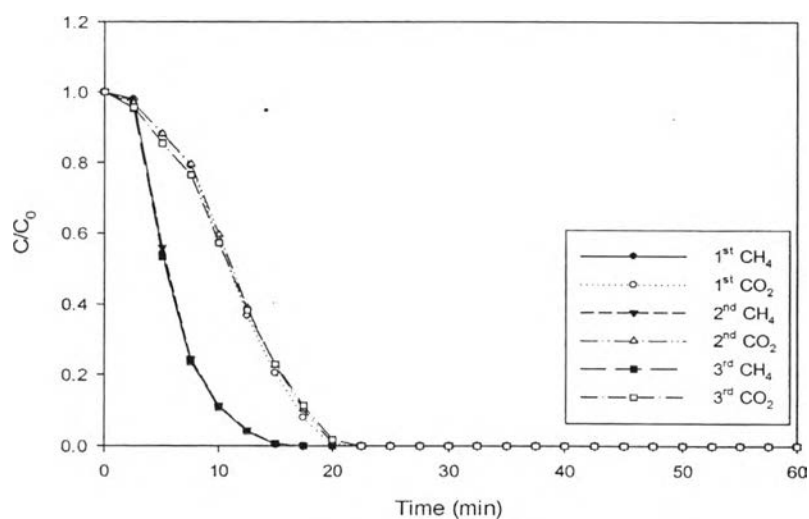
**Figure 4.23** Breakthrough curves of methane and carbon dioxide from the 3-cycle adsorption process on the CSAC treated by potassium hydroxide and modified by 0.010 wt% MTES at room temperature.



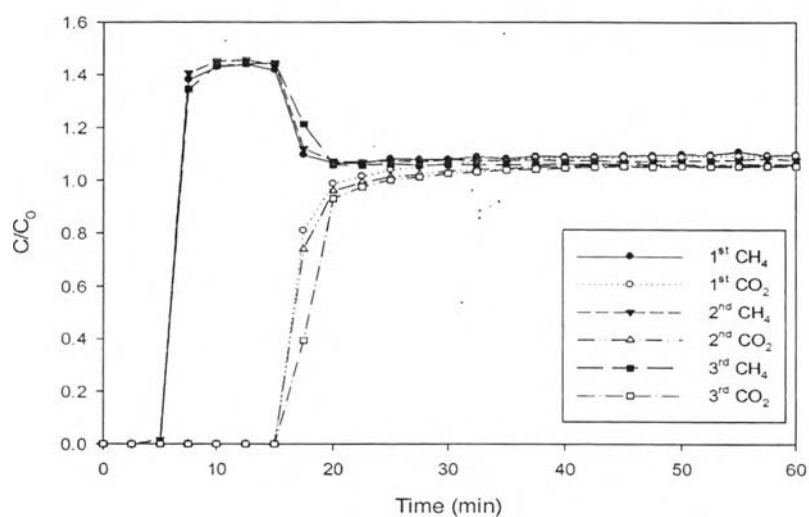
**Figure 4.24** Three desorption cycles of methane and carbon dioxide on the CSAC treated by potassium hydroxide and modified by 0.010 wt% MTES at room temperature.



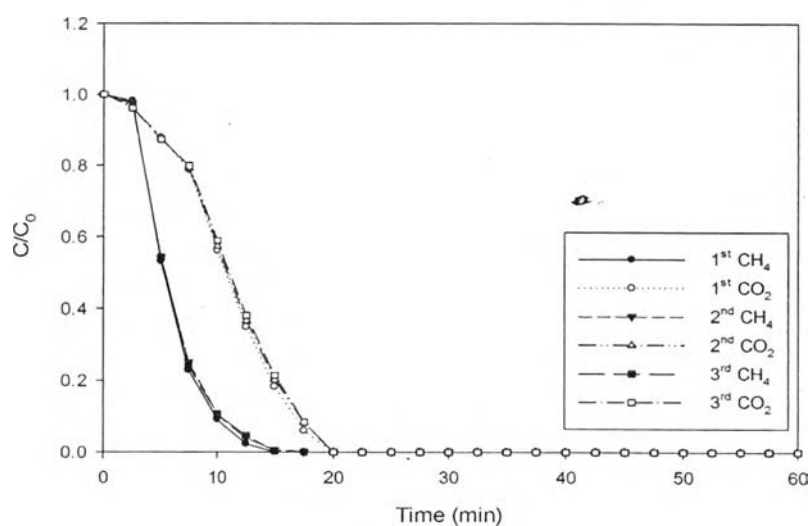
**Figure 4.25** Breakthrough curves of methane and carbon dioxide from the 3-cycle adsorption process on the CSAC treated by potassium hydroxide and modified by 0.020 wt% MTES at room temperature.



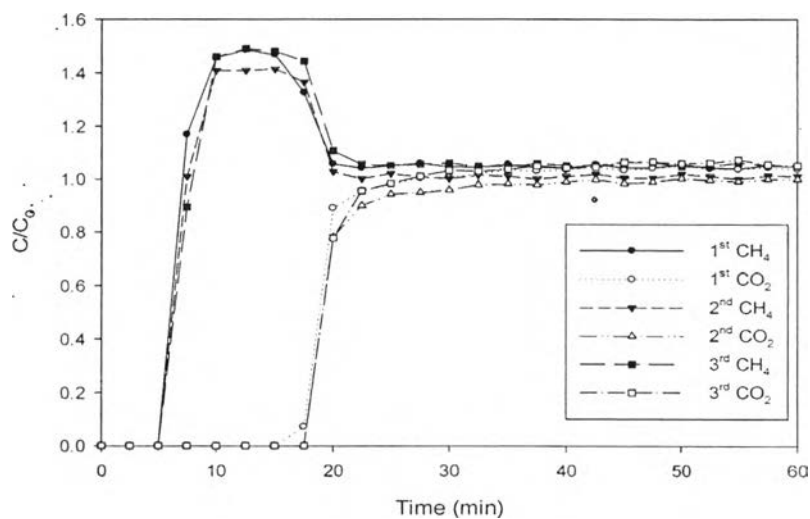
**Figure 4.26** Three desorption cycles of methane and carbon dioxide on the CSAC treated by potassium hydroxide and modified by 0.020 wt% MTES at room temperature.



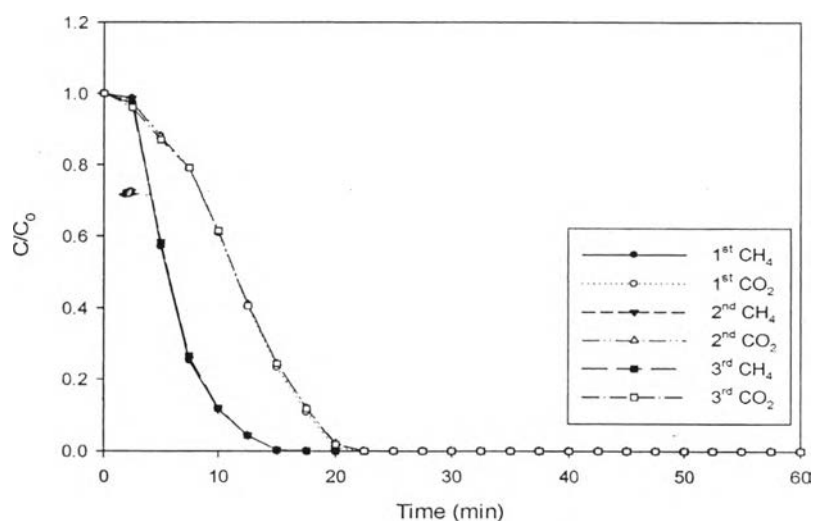
**Figure 4.27** Breakthrough curves of methane and carbon dioxide from the 3-cycle adsorption process on the CSAC treated by potassium hydroxide and modified by 0.030 wt% MTES at room temperature.



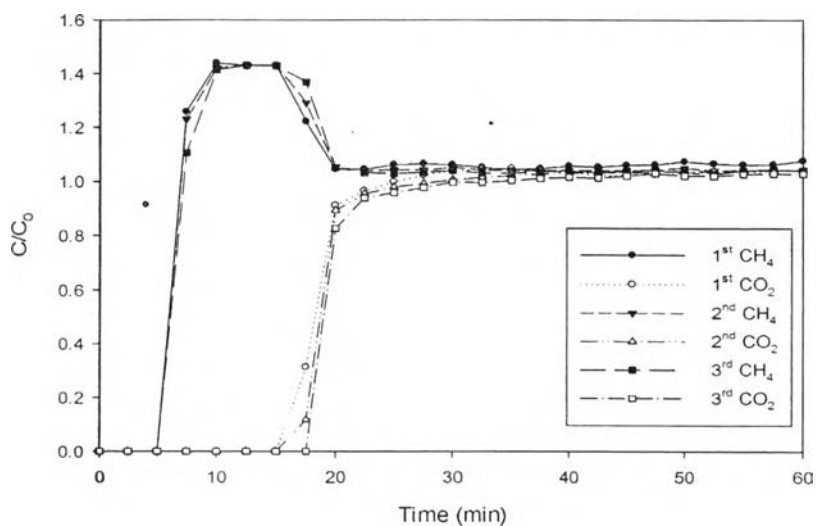
**Figure 4.28** Three desorption cycles of methane and carbon dioxide on the CSAC treated by potassium hydroxide and modified by 0.030 wt% MTES at room temperature.



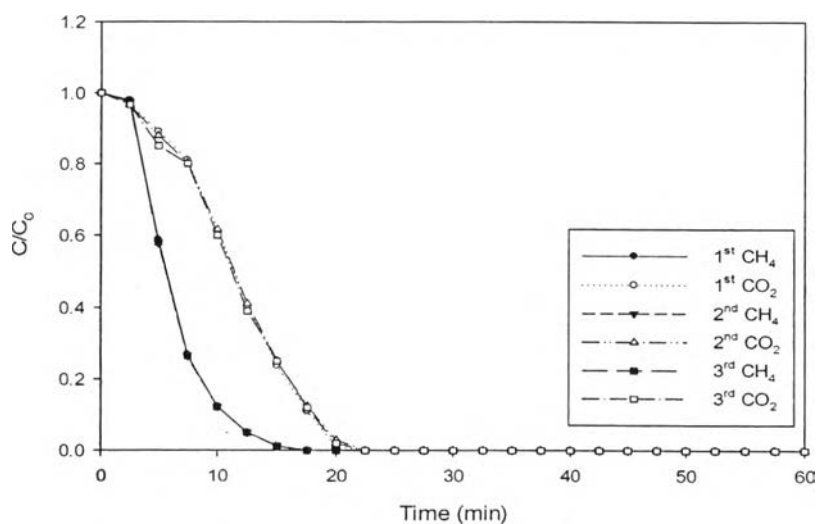
**Figure 4.29** Breakthrough curves of methane and carbon dioxide from the 3-cycle adsorption process on the CSAC treated by ammonium hydroxide and modified by 0.005 wt% MTES at room temperature.



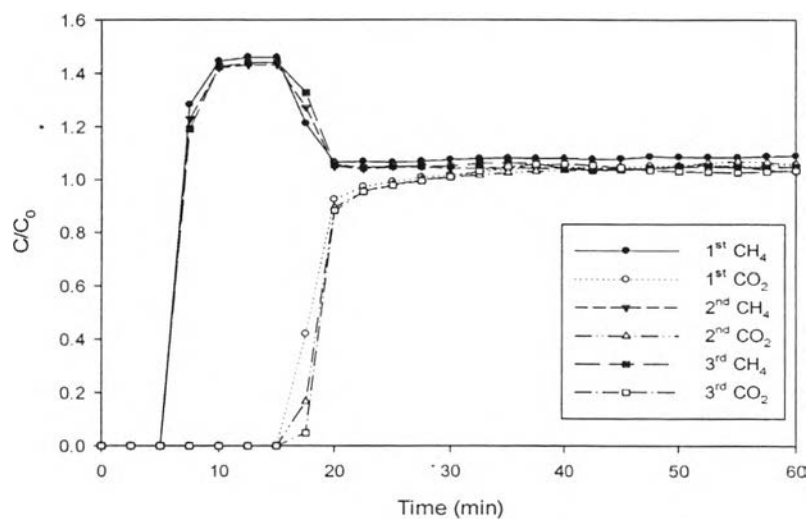
**Figure 4.30** Three desorption cycles of methane and carbon dioxide on the CSAC treated by ammonium hydroxide and modified by 0.005 wt% MTES at room temperature.



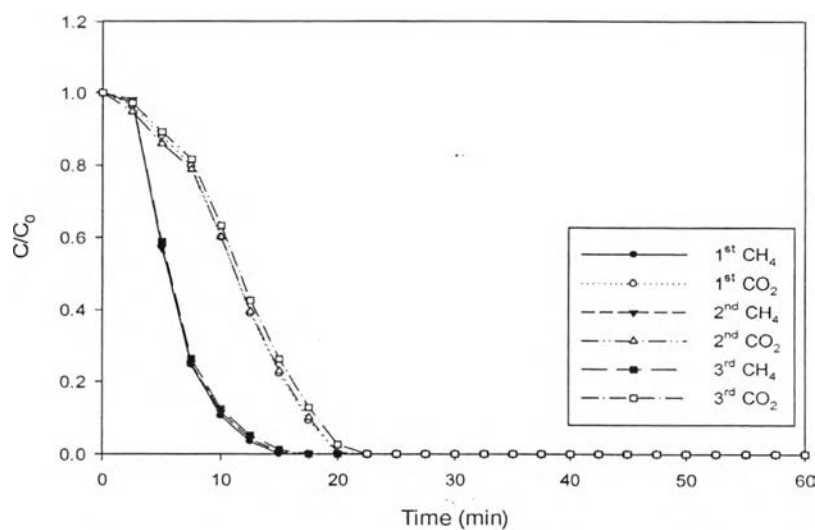
**Figure 4.31** Breakthrough curves of methane and carbon dioxide from the 3-cycle adsorption process on the CSAC treated by ammonium hydroxide and modified by 0.010 wt% MTES at room temperature.



**Figure 4.32** Three desorption cycles of methane and carbon dioxide on the CSAC treated by ammonium hydroxide and modified by 0.010 wt% MTES at room temperature.

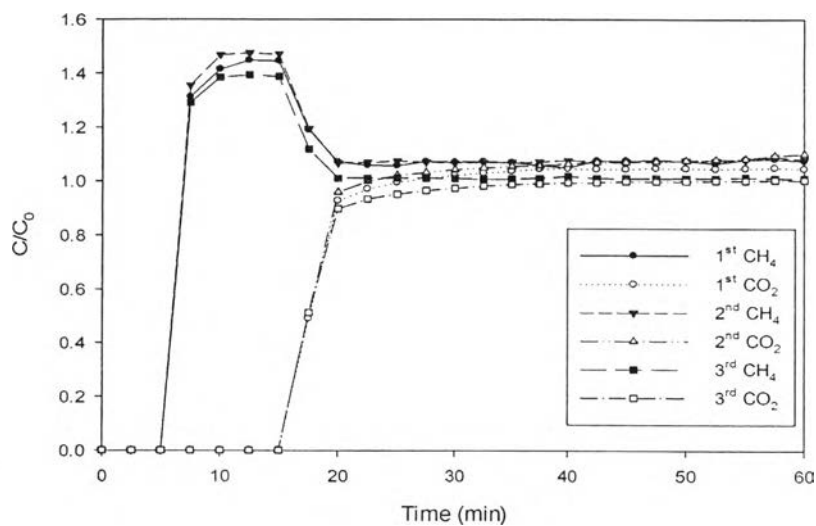


**Figure 4.33** Breakthrough curves of methane and carbon dioxide from the 3-cycle adsorption process on the CSAC treated by ammonium hydroxide and modified by 0.020 wt% MTES at room temperature.

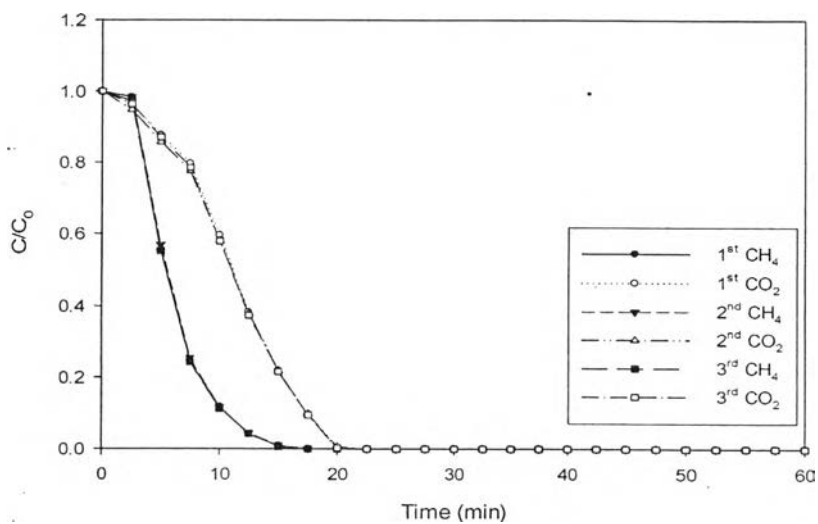


**Figure 4.34** Three desorption cycles of methane and carbon dioxide on the CSAC treated by ammonium hydroxide and modified by 0.020 wt% MTES at room temperature.





**Figure 4.35** Breakthrough curves of methane and carbon dioxide from the 3-cycle adsorption process on the CSAC treated by ammonium hydroxide and modified by 0.030 wt% MTES at room temperature.



**Figure 4.36** Three desorption cycles of methane and carbon dioxide on the CSAC treated by ammonium hydroxide and modified by 0.030 wt% MTES at room temperature.

For the breakthrough time of carbon dioxide, the results indicate that the stability of CSAC treated by potassium hydroxide and modified with 0.010% MTES increases from 15 to 17.5 min in the last cycle, which is the same trend for the CSAC treated by ammonium hydroxide and modified with 0.005 and 0.010% MTES. The breakthrough times of carbon dioxide increase due to the adsorbent might lost its ability to adsorb gases after adding the MTES. Some gas molecules from the first and the second cycle may adsorb in the pores resulting in a longer time to equilibrate its surface. Another reason may be because the carbon dioxide molecules preferentially adsorb on all the adsorbents resulting in the difficulty to desorb the carbon dioxide molecules.

#### 4.2.3 Methane and Carbon Dioxide Adsorption Capacity

The adsorption capacity was estimated from the breakthrough curves using Eq. (4.1):

$$Q_{ads} = \frac{FC_0t_g}{W} \quad (4.1)$$

where  $Q_{ads}$  is adsorption capacity of any gas in mole/g,  $F$  is gas flow rate in mole/minute,  $C_0$  is initial concentration of gas in mole,  $t_g$  is integrating time in minute, calculated from Eq. (4.2) (Geankoplis, 1993), and  $W$  is weight of adsorbent in g.

$$t_g = \int_0^{\infty} \left(1 - \frac{C}{C_0}\right) dt \quad (4.2)$$

where  $C$  is concentration at any time in mole.

After determining the adsorption capacity of  $CO_2$  and  $CH_4$ , the ideal selectivity of the adsorbent as its ability criterion in adsorption process was calculated using Eq. (4.3)

$$\text{Adsorption selectivity} = \frac{n_{CH_4}}{n_{CO_2}} \quad (4.3)$$

**Table 4.3** Summary of adsorption capacity, and selectivity of investigated CSACs

Adsorbent	CH <sub>4</sub> adsorption (mmol/g)	CO <sub>2</sub> adsorption (mmol/g)	Total adsorption (mmol/g)	CH <sub>4</sub> selectivity
CASC	0.58	2.87	3.45	0.20
CSAC – 0.005%MTES	0.61	2.81	3.42	0.22
CSAC – 0.010%MTES	0.60	2.70	3.30	0.22
CSAC – 0.020%MTES	0.59	2.57	3.16	0.23
CASC – 0.030%MTES	0.57	2.52	3.09	0.23
KOH/CSAC	0.72	2.98	3.70	0.24
KOH/CSAC – 0.005%MTES	0.70	2.88	3.58	0.24
KOH/CSAC – 0.010%MTES	0.71	2.84	3.55	0.25
KOH/CSAC – 0.020%MTES	0.68	2.83	3.51	0.24
KOH/CSAC – 0.030%MTES	0.56	2.55	3.11	0.22
NH <sub>4</sub> OH/CSAC	0.82	3.00	3.82	0.27
NH <sub>4</sub> OH/CSAC – 0.005%MTES	0.81	2.89	3.70	0.28
NH <sub>4</sub> OH/CSAC – 0.010%MTES	0.73	2.85	3.58	0.26
NH <sub>4</sub> OH/CSAC – 0.020%MTES	0.68	2.83	3.51	0.24
NH <sub>4</sub> OH/CSAC – 0.030%MTES	0.66	2.78	3.44	0.24

From Table 4.3, the total adsorption of original CSAC is 3.45 mmol/g with 0.58 mmol/g and 2.87 mmol/g. The adsorption of methane increases dramatically from 0.58 mmol/g to 0.72 mmol/g for the CSAC treated by potassium hydroxide and 0.82 mmol/g for CSAC treated by ammonium hydroxide. It was reported that the oxygen-containing group was decreased after an alkali treatment (Li *et al.*, 2011). That may be a reason why the methane adsorption on the CSAC treated by potassium hydroxide and the CSAC treated by ammonium hydroxide increases. After the modification with MTES, the methane adsorption decreases slightly with increasing the MTES concentration. Moreover, carbon dioxide adsorption decreases after increasing the MTES concentration. Because some oxygen containing groups

are neutralized resulting in the hydrophobic extent on the surface. The hydrophobicity on the adsorbent surface improves the methane adsorption capacity because the methane molecule is a hydrophobic molecule unlike the carbon dioxide molecule, which is a hydrophilic molecule.

The adsorption selectivity of methane over carbon dioxide on the investigated adsorbents shows that the addition of 0.020 wt% and 0.030 wt% MTES onto the untreated CSAC gives the high selectivity is 0.23. For the CSAC treated by potassium hydroxide and modified by MTES, the highest methane selectivity is 0.25 with 0.010 wt% MTES. Although the methane adsorption decreases compared with the KOH/CSAC, the carbon dioxide adsorption decreases dramatically more than the methane adsorption. For the CSAC treated by ammonium hydroxide and modified by MTES, the highest of methane selectivity is 0.28 with 0.005 wt% MTES.